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# Ion Beam Modification of Polymethyl methacrylate (PMMA) Polymer Matrix Filled with Organometallic Complex

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A Nickel Dimethylglyoxime (Ni-DMG) compound was dispersed in polymethyl methacrylate (PMMA) films at different concentrations. PMMA was synthesized by a solution polymerization technique. These films were irradiated with 120 MeV Ni<sup>10+</sup> ions at the fluences of  $1 \times 10^{11}$  and  $1 \times 10^{12}$  ions/cm<sup>2</sup>. The radiation induced changes in dielectric properties and average surface roughness were investigated by using an LCR meter in the frequency range 50 Hz to 10 MHz and atomic force microscopy (AFM), respectively. The electrical properties of irradiated films are found to increase with the fluence and also with the concentration of Ni-DMG. From the analysis of frequency,  $f$ , dependence of dielectric constant,  $\epsilon$ , it has been found that the dielectric response in both pristine and irradiated samples obey the Universal law given by  $\epsilon \propto f^{n-1}$ . The dielectric constant/loss is observed to change significantly due to the irradiation. This suggests that ion beam irradiation promotes (i) the metal to polymer bonding (ii) convert the polymeric structure in to hydrogen depleted carbon network due to the emission of hydrogen gas and/or other volatile gases. Atomic force microscopy (AFM) shows that the average surface roughness and surface morphology of irradiated films are observed to change.

**Keywords:** PMMA; composites; ion irradiation; AC electrical frequency response; AFM

## 1 Introduction

Polymer composites filled with metal fillers result in a unique combination of thermal, mechanical and electrical properties, which make them useful for various applications. By introducing suitable fillers in polymers, composite properties can be tailored to meet specific design requirements such as low density, high strength, high stiffness, high damping, chemical resistance, thermal shock resistance, high thermal conductivity, low coefficient of thermal expansion (CTE) and good electrical properties such as dielectric constant. Composite materials of an amorphous polymeric matrix and randomly dispersed metal particles are considered as heterogeneous disordered systems (1–3). The electrical performance of granular materials, as these systems are sometimes referred to, is directly related to the permittivity and conductivity of the constituent phases, the size, shape and volume fraction of the inclusions and can be experimentally investigated by

means of dielectric spectroscopy (DS) and dc conductivity measurements (4–11). Other important factors could be the adhesion between the host medium and the inclusions, the method of processing and possible interactions between the conductive and nonconductive phases (12, 13). Polymers and polymer matrix composites are basically electrical insulators, due to their low concentration of free charge carriers. Thus, their electrical response is, mainly, associated with relaxation phenomena occurring under the influence of an AC field. The observed relaxation processes are related to dipolar orientation effects or space charge migration (3, 14). Molecular mobility and interfacial polarization are regarded as the origin of dielectric effects.

The high energy ion irradiation effects in polymers have attracted considerable attention for applications of polymers in radiation environment and also in the development of new electronic devices (15, 16). The swift heavy ions slow down in the matter and lose their energy mainly via electronic excitations and ionizations. The deposited energy may be converted into atomic motion and finally leads to the structural and chemical modifications within a cylindrical zone of several nanometers in diameter (17, 18) and new structural arrangements may emerge (19, 20). Ion beam irradiation has long been

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recognized as an effective method for modifying the properties of diverse materials, including polymers and polymer composites. Important properties of polymer composites i.e. mechanical property, thermal stability, chemical resistance, melt flow, process ability and surface properties significantly improved by ion beam irradiation (21–23). In this study, organometallic complex was dispersed at different concentrations in PMMA matrix and irradiated with 120 MeV, Ni<sup>10+</sup> ions at the fluences of  $1 \times 10^{11}$  and  $1 \times 10^{12}$  ions/cm<sup>2</sup>. The radiation induced changes in dielectric properties and surface morphology were studied by means of LCR meter and atomic force microscopy, respectively.

## 2 Experimental

Nickel dimethylglyoxime (Ni-DMG) compound was formed by dissolving 0.4 mole nickel chloride in 200 ml water and it was heated at 80°C; a slight excess of the alcoholic dimethylglyoxime (DMG) was added and then dilute ammonia solution was added drop wise with continuous stirring until precipitation took place. The precipitate was then washed with cold water until free from Cl<sup>-</sup> and dried at 110°C for 1 h. PMMA was prepared by solution polymerization method. In this method, benzoyl peroxide (BPO; 0.8 g; an initiator for polymerization) was dissolved in fresh inhibitor-free MMA (80 ml methyl methacrylate) monomer, with ethyl acetate as a solvent (80 ml) in a round bottom flask; the solution was then refluxed for 5 h at 80°C temperature in the hot water bath. The resulting solution was then precipitated out in another beaker containing methanol (100 ml). The PMMA, precipitated out in methanol, was dried at room temperature for 2 h. The polymerized PMMA and Ni-DMG compound of 5%, 20%, and 40% were dissolved using toluene; acetone (50:40) and Briz-35 surfactant (0.5 at % of the polymer) the solutions were mixed and stirred thoroughly for about an hour and then poured into a clean glass trough. The solvent was evaporated at room temperature (25°C ± 1°C) to get thin films (thickness ~100 μm) of dispersed PMMA with 5%, 20%, and 40% concentration of Ni-DMG compound. The 1.5 × 1.5 cm<sup>2</sup> size films were cut and used for irradiation. All films were irradiated with 120 MeV Ni<sup>10+</sup> ions at the fluences of 10<sup>11</sup>, and 10<sup>12</sup> ions/cm<sup>2</sup> from the Pelletron of the Inter University Accelerator Center (IUAC), New Delhi, India. AC electrical properties of all samples were measured in the frequency range 50 Hz – 10 MHz at room temperature using a variable frequency LCR meter (General Radio, USA; model-1689; model-1689/Hewlett Packard 4284A). Electrical contact on the sample was made by applying an air drying type of silver paste, and then the sample was mounted between the two electrodes

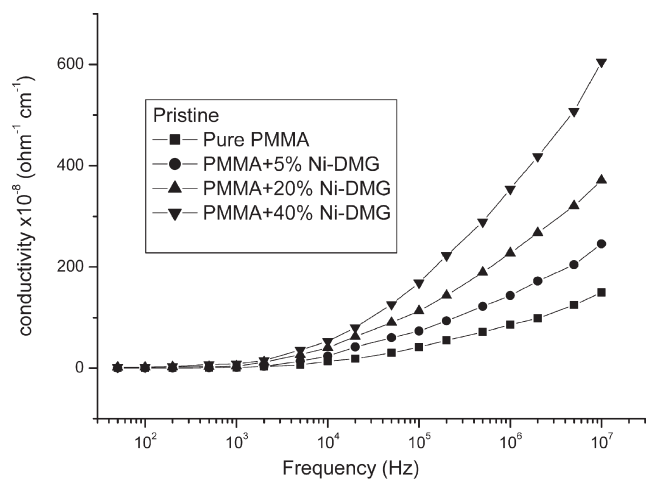
(diameter 8 mm) of sample holder. The conductivity of the material was calculated using the relation  $\sigma = 2\pi f C_p D t / A$  (Ω·cm)<sup>-1</sup> and dielectric permittivity  $\epsilon = C_p / C_o$ .

Where C<sub>p</sub> is the capacitance measured using an LCR meter, f the frequency, D dielectric loss and C<sub>o</sub> = ε<sub>o</sub>A/t, A and t are the cross sectional area of the electrode and thickness of the sample, respectively. ε<sub>o</sub>: permittivity of vacuum = 8.85 × 10<sup>-12</sup> F/m. The surface morphology of pristine and irradiated surfaces was studied using an atomic force microscope (AFM) in the contact mode (Digital Nanoscope IIIa Instrument Inc.)

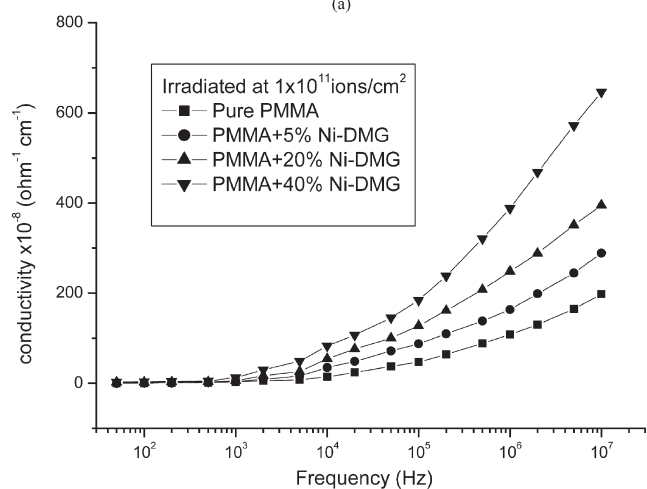
## 3 Results and Discussion

### 3.1 AC Electrical Frequency Response

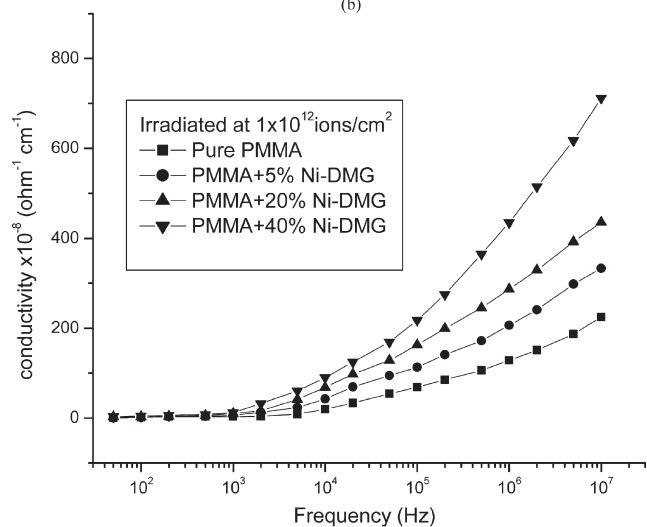
AC electrical measurement was performed for pristine and irradiated samples. Figure 1 (a, b, and c) shows the variation of conductivity with log of frequency for the pristine and irradiated samples at different Ni-DMG concentrations. The conductivity was observed to increase in pristine as well as irradiated samples. It was also observed that conductivity increases with increasing concentration of dispersed Ni-DMG compound (Figure 1a, pristine) as well as those irradiated at the fluence of  $1 \times 10^{11}$  ions/cm<sup>2</sup> (Figure 1b) and  $1 \times 10^{12}$  ions/cm<sup>2</sup> (Figure 1c), respectively. The increase in conductivity with different Ni-DMG concentrations for pristine samples may be attributed to the conductive phase formed by dispersed organometallic compound in polymer matrix. It is known that electrical conductivity of such composites depends on the type and concentration of the dispersed compound (24, 25). As a result the conductivity of dispersed films increases on increasing the concentration of Ni-DMG compound in the polymer matrix. It is also observed that after the irradiation the conductivity increases with fluence (Figure 1). Irradiation is expected to promote the metal to polymer bonding and convert the polymeric structure in to a hydrogen depleted carbon network. It is this carbon network that is believed to make the polymers more conductive (26). Figure 2 (a, b, and c) shows the plot of dielectric constant versus log frequency for pristine and irradiated samples of pure PMMA and different concentrations of Ni-DMG dispersed PMMA films. When the fillers are dispersed in the insulating polymer, the dielectric constant of composites investigated increases with concentration of fillers. Such results have been observed experimentally (27, 28). The partial agglomerations also increase with increasing the filler concentration as shown in Figure 4 (AFM). As evident from Figure 2, the dielectric constant remains almost constant up to 100 kHz. At these frequencies, the motion of the free charge carriers is constant and so the dielectric



(a)

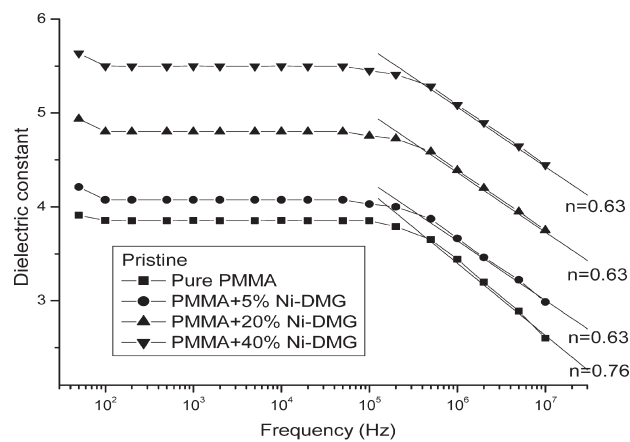


(b)

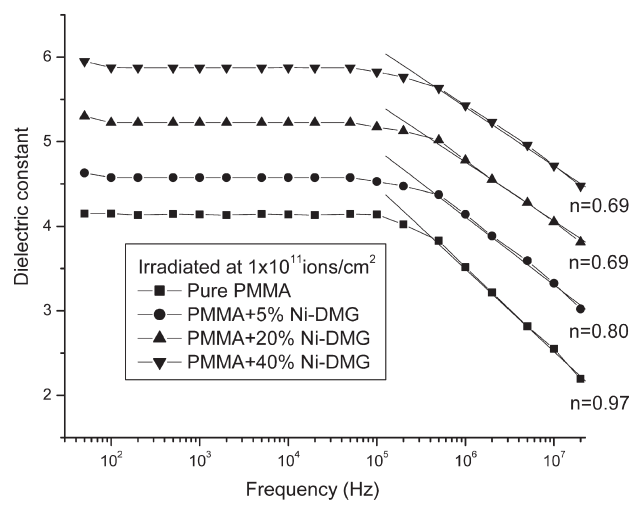


(c)

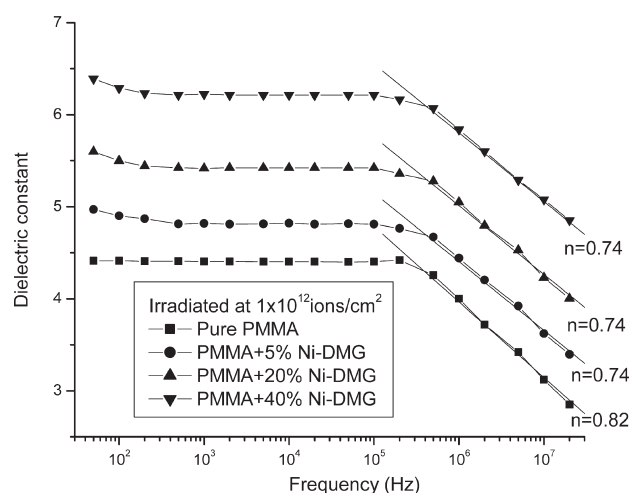
**Fig. 1.** (a) AC conductivity versus log frequency for pristine pure and dispersed Ni-DMG in PMMA films; (b) AC conductivity vs. log frequency for irradiated (at the fluence of  $1 \times 10^{11}$  ions/cm<sup>2</sup>) pure and dispersed Ni-DMG in PMMA films; (c) AC conductivity vs. log frequency for irradiated (at the fluence of  $1 \times 10^{12}$  ions/cm<sup>2</sup>) pure and dispersed Ni-DMG in PMMA films.



(a)



(b)



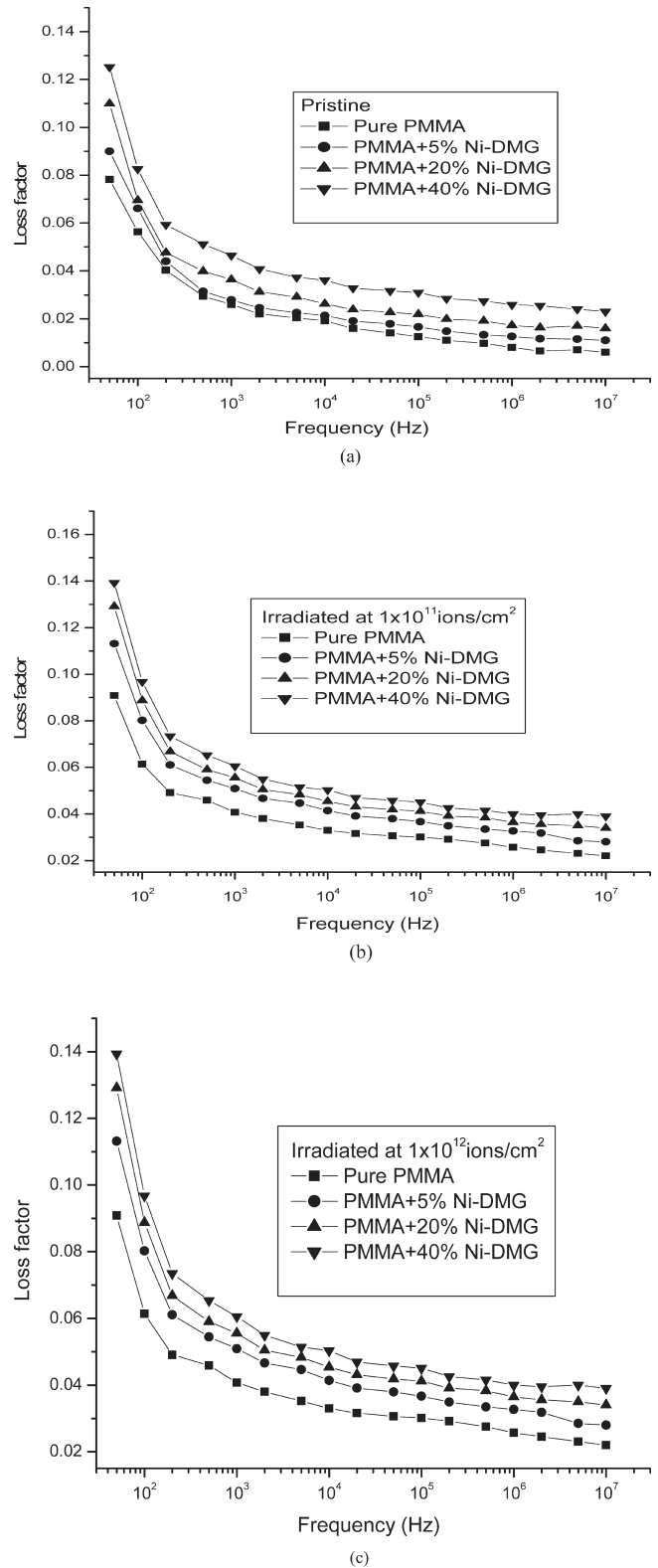
(c)

**Fig. 2.** (a) Plot of dielectric constant vs. log frequency for pristine pure and dispersed Ni-DMG in PMMA films; (b) Plot of dielectric constant vs. log frequency for irradiated (at the fluence of  $1 \times 10^{11}$  ions/cm<sup>2</sup>) pure and dispersed Ni-DMG in PMMA films; (c) Plot of dielectric constant vs. log frequency for irradiated (at the fluence of  $1 \times 10^{12}$  ions/cm<sup>2</sup>) pure and dispersed Ni-DMG in PMMA films.

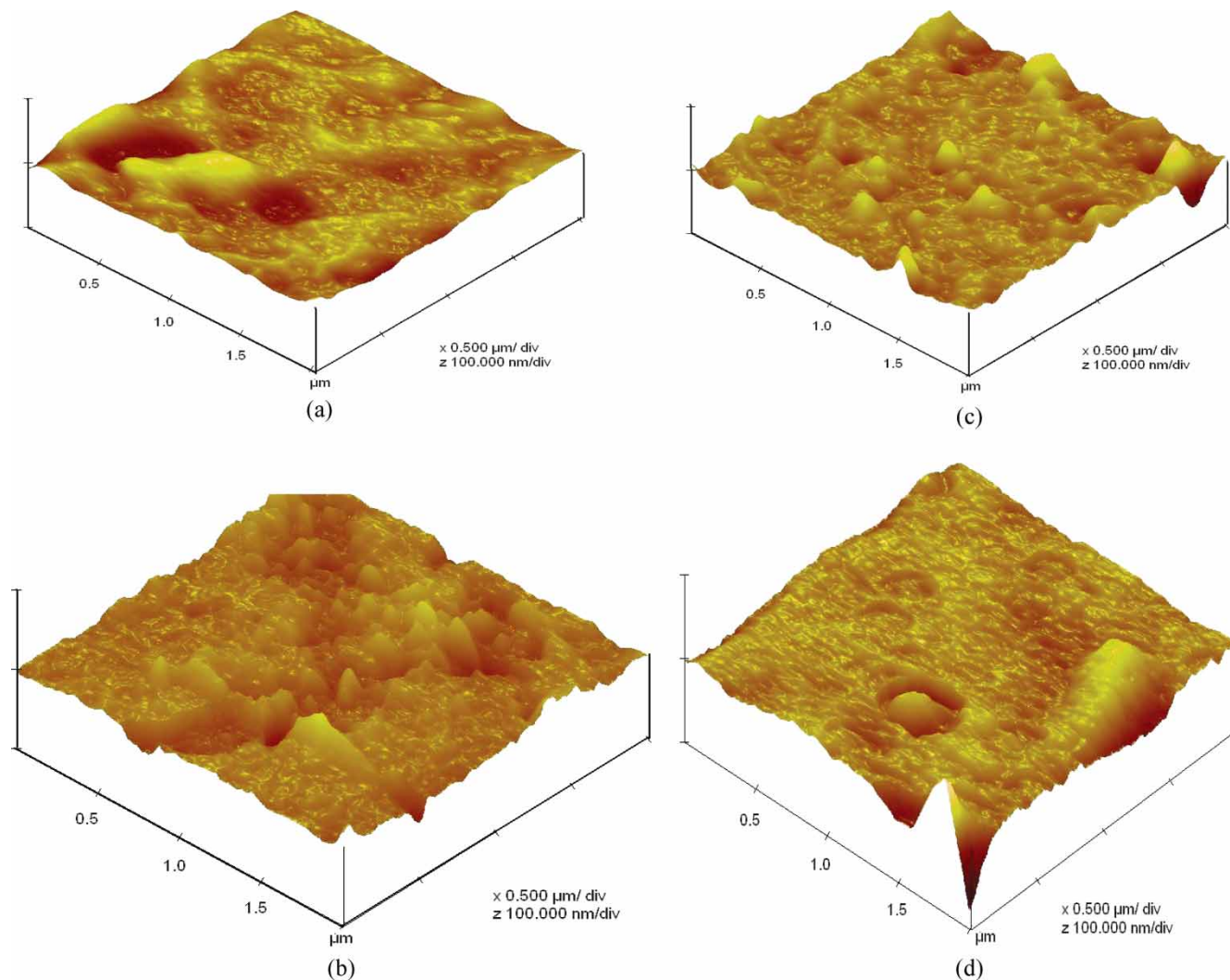
constant presumably remains unchanged. It is also observed that dielectric constant increases for irradiated films with fluence. The increase in dielectric constant may be attributed to the chain scission and as a result the increase in the number of free radicals, unsaturation etc. As frequency increases further (i.e., beyond 100 kHz), the charge carriers migrate through the dielectric and get trapped against a defect sites and induced an opposite charge in its vicinity. At these frequencies, the polarization of trapped and bound charges can not take place and hence the dielectric constant decreases (29). The dielectric constant decreases at higher frequencies (i.e., beyond 100 kHz) obeys the universal law (30) of dielectric response given by  $\epsilon \propto f^{n-1}$ , where  $n$  is power law exponent and varies from zero to one ( $0 < n < 1$ ),  $n = 0.76$  for pure PMMA, 0.63 for 5%, 20% and 40% Ni-DMG dispersed pristine films were observed respectively. The value of  $n = 0.97$  and 0.82 for pure PMMA; 0.80 and 0.74 for 5%; 0.69 and 0.74 for 20% and 0.69 and 0.74 for 40% dispersed Ni-DMG dispersed irradiated samples were obtained at the fluences of  $1 \times 10^{11}$  ions/cm<sup>2</sup> (Figure 2b) and  $1 \times 10^{12}$  ions/cm<sup>2</sup> (Figure 2c), respectively. The Figure 2 (a, b, and c) clearly shows that the frequency dependence of dielectric constant,  $\epsilon$ , obeys Universal law. The observed nature of the fluence dependence of dielectric constant in studied frequency range can be explained by the prevailing influence of the enhanced free carriers due to irradiation (31). Figure 3 (a, b, and c) shows the variation of dielectric loss with log frequency for pristine and irradiated samples of pure PMMA and Ni-DMG dispersed PMMA films at the concentration of 5%, 20%, and 40%, respectively. The dielectric loss decreases exponentially with the increase of log frequency. It is noticed that dielectric loss increases with the concentration of filler and also with the fluence.

### 3.2 Morphology of the Composites

The surface morphology of pristine and irradiated films of pure PMMA, and 40% Ni-DMG dispersed PMMA films was measured by AFM on a  $2 \times 2 \mu\text{m}^2$  area as shown in Figure 4. Each AFM image was analyzed in terms of surface average roughness (Ra). The average roughness values are 4.9 nm and 14 nm for unirradiated samples and those of 2 nm and 4.6 nm for irradiated samples at the fluence of  $1 \times 10^{12}$  ions/cm<sup>2</sup>. It was found that roughness increases as Ni-DMG concentration increases. The increase in roughness may be due to the increase of density and size of metal particles on the surfaces of the PMMA films (32, 33). It is also observed that after irradiation the roughness of the surface decreases and the surface becomes significantly smoother. This relative smoothness is probably due to defect enhanced surface diffusion.



**Fig. 3.** a) Plot of dielectric loss vs. log frequency for pristine pure and dispersed Ni-DMG in PMMA films; (b) Plot of dielectric loss vs. log frequency for irradiated (at the fluence of  $1 \times 10^{11}$  ions/cm<sup>2</sup>) pure and dispersed Ni-DMG in PMMA films; (c) Plot of dielectric loss vs. log frequency for irradiated (at the fluence of  $1 \times 10^{12}$  ions/cm<sup>2</sup>).



**Fig. 4.** (a) AFM image of pure PMMA film (pristine); (b) AFM image of dispersed Ni-DMG (40%) in PMMA film (pristine); (c) AFM image of pure PMMA film (irradiated at the fluence of  $\times 10^{12}$  ions/cm<sup>2</sup>); (d) AFM image of dispersed Ni-DMG (40%) in PMMA film (irradiated at the fluence of  $1 \times 10^{12}$  ions/cm<sup>2</sup>).

#### 4 Conclusions

From this study, it is observed that dielectric property of organometallic compound dispersed PMMA films is greatly enhanced by ion beam irradiation. It may be attributed to (i) metal to polymer bonding and (ii) conversion of the polymeric structure to hydrogen depleted carbon network. Thus, irradiation makes the polymer more conductive. Dielectric loss and constant are observed to change significantly with the fluence. This might be attributed to breakage of chemical bonds and resulting in the increase of free radicals, unsaturation, etc. It is also observed that dielectric constant obeys Universal law of dielectric response. The surface roughness increases as Ni-DMG concentration increases but decreases on irradiation as observed from AFM studies.

#### 5 Acknowledgments

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